FINAL REPORT

Project Title: Systematic Evaluation of Jc Decrease in Thick Film Coated Conductors

Covering Period: October 1, 2003 through December 31, 2003

Date of Report: May 10, 2006

Recipient: Texas Center for Superconductivity and Advanced Materials
University of Houston
202 UHSC
Houston, TX 77204-5002

Award Number: DE-FC07-03ID14512

Subcontractors: None

Other Partners: None

Contact(s): Alex Ignatiev
713-743-3630 phone
713-747-7724 FAX
Ignatiev@uh.edu

Project Team: Dr. Amit Goyal, Oak Ridge National Labs

Project Objective: We proposed to address both the thickness dependence of Jc, in thick film YBCO coated conductors through an application of a suite of new measurement techniques to thick film wire samples produced by commercially viable coated conductor technologies. We proposed to fabricate a series of thick film YBCO samples (from 0.5 to 8 ?m thickness) on oxide and RABiTS substrates by high growth rate photo assisted MOCVD. The oxide substrates, although not commercially viable, will play an important role in helping to better elucidate the Jc vs. thickness problem by partially eliminating the question of quality of cube texturing of the substrate. The Proposed Objectives were only partially fulfilled due to premature termination of funding of the 3-year program after **only the first year**.

Background: The development of second generation coated conductor high temperature superconducting wire has significantly moved forward in the past two to three years. However, a challenge still exists with respect to the attainment of high Jc values for thick YBCO films that are expected to be used in production versions of the coated conductor wire. The use of YBCO films for high current applications dictates thick films (~5 ?m) so as to yield wire currents of >500 - 800A for wire widths of ? 1cm. In coated conductors, however, for large thicknesses (> 1?m), it has been identified that Jc drops nearly exponentially with increasing thickness. As a result, it is important to attempt to understand and mitigate this problem with the result of realizing high current thick film coated conductors.

Results: Thick YBCO films were grown by photo-assisted MOCVD on $LaAlO_3$ (LAO) substrates. The growths at the beginning of eth contract resulted in poor quality YBCO films with extensive particles and poor crystalline quality. It was determined that the MOCVD system was dirty and required renovation before high quality films were possible due to extensive particulate contamination in the system. The disassembly and cleaning was completed in late November with growths re-initiated by December 1. Thick YBCO film growth on LAO was initially attempted with excellent results. The third growth in the system yielded YBCO films of ~ 4 µm thickness with very high density with no observable voids under SEM as can be seen in Figure 1. The YBCO films also had good surface morphology with some protuberances that were less than the thickness of the film and were shown by TEM analysis to be ON TOP of the YBCO and in the YBCO. XRD analysis showed extremely high order with the f -scan FWHM of less than 1.8^o as seen in Figure 2. Tc measurement showed a 91K value, and the Jc measurement yielded a value of greater than 6 x 10^5A/cm^2 for a **4 µm thick** YBCO film. Further measurements are being made on this thick film to corroborate the 0.6MA/cm^2 number and understand its low value.

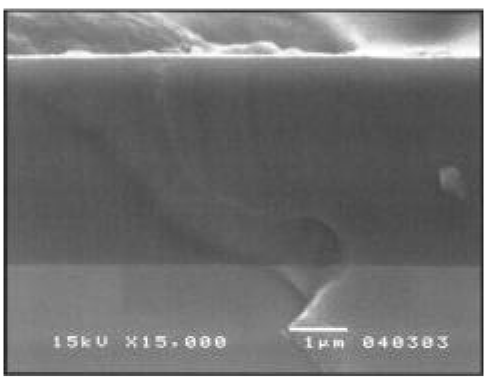


Figure 1. 4µ thick YBCO film on LAO

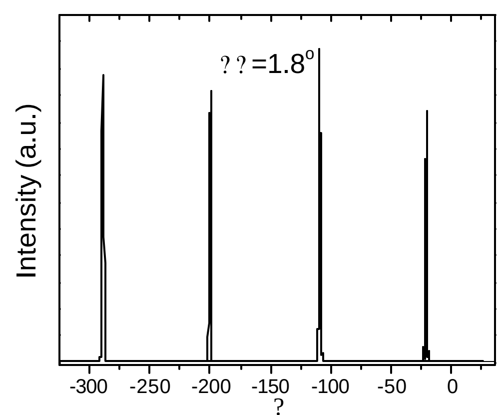
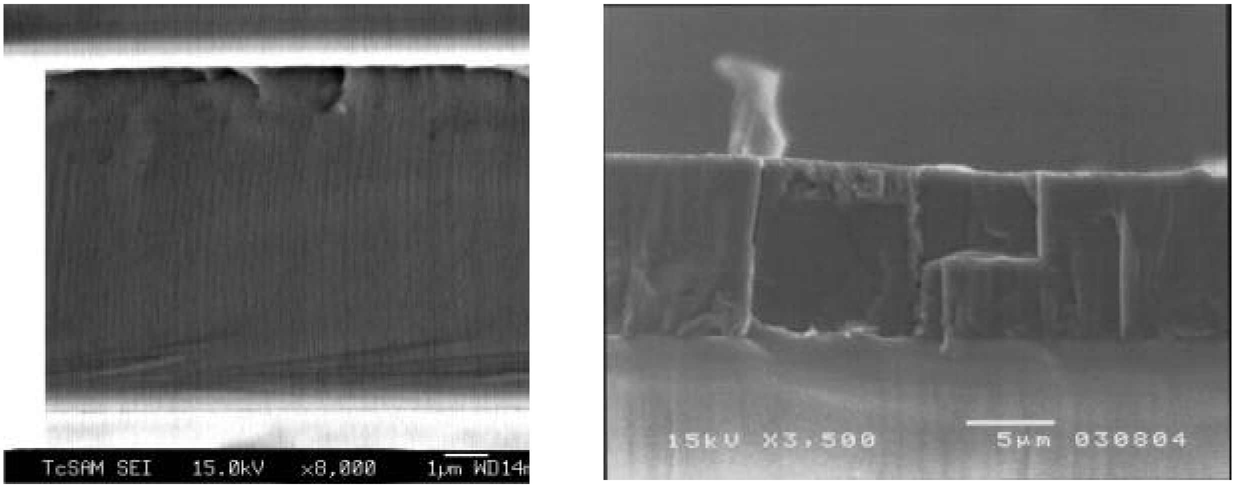


Figure 2. f -scan of 4µ thick YBCO film on LAO

Additional recent thick YBCO film growth has resulted in a series of YBCO films from 3 to 10 µm thickness. The YBCO were grown by photo-assisted MOCVD on $LaAlO_3$ (LAO) substrates utilizing both single precursor source delivery and multiple precursor source delivery. Both systems gave similar quality films and both have been able to grown thick films. The current growth rates have been conservative at about 0.2 – 0.3 µm per minute. Higher growth rates have previously been shown to be effective, and will be used in future work.

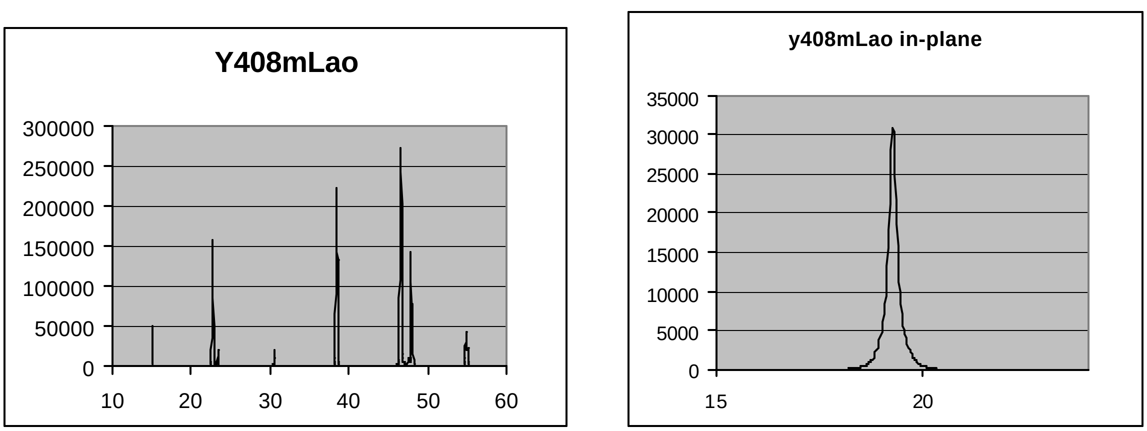
The intriguing part of the work is that the thick film samples have all been grown with high crystalline quality. Figure 3 shows the SEM for two thick YBCO samples (9 µm and 10 µm). It is well to note that the density of the films is high throughout the film thickness with a minimum of observed macro-defects.



a. b.

Figure 3. Micrographs of the cross section of two YBCO thick films. Note uniform density of films.

Detailed study of the microstructure of the films reveled an exceptionally high degree of atomic order as seen from the XRD data of Figure 4.



a. b.

Figure 4. XRD spectra for YBCO sample 1a. FWHM of figure b. is 0.25 ^{o}.

Additional XRD GADDS data of Figure 5 confirm excellent pole figures with ? FWHM of 2^{o}.

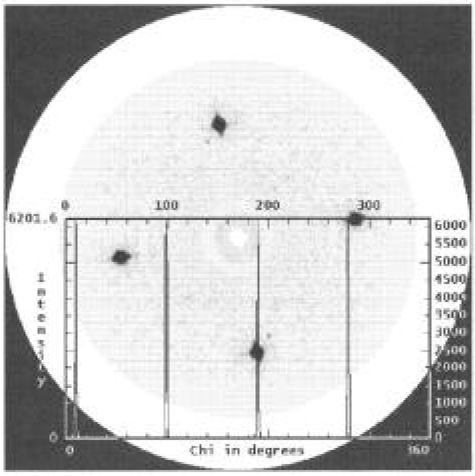
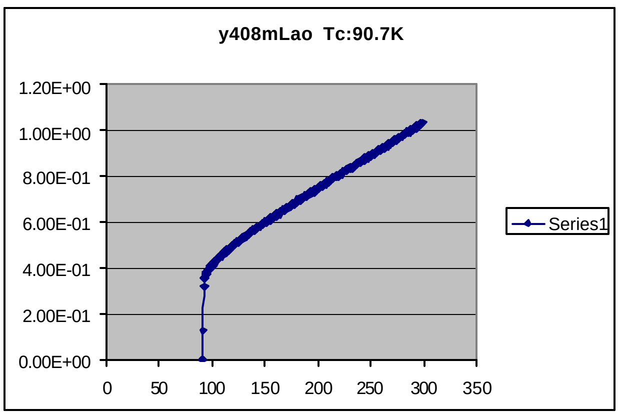
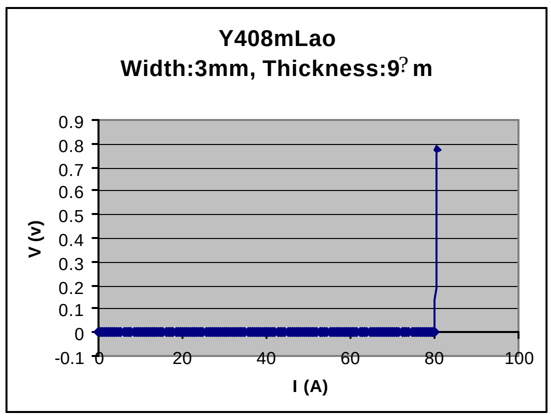


Figure 5. GADDS rotation diagram of the YBCO sample of Figure 1a.

The superconducting properties of the samples have been measured, and to a sample, the Tc's are quite good at 91-92K as seen in Figure 6a, but the Jc's are low: ~2-4 x 10^5 A/cm^2 as seen in Figure 6b for the sample of Figure 1a..



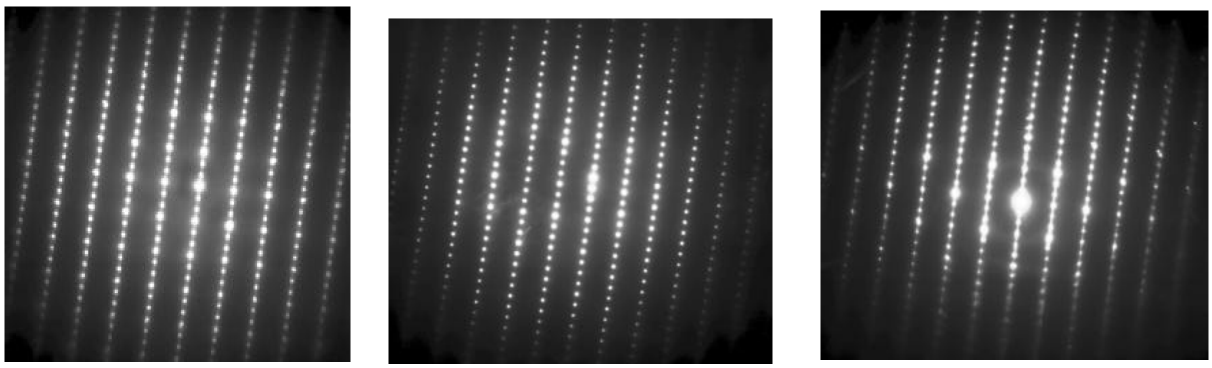
a.



b.

Figure 6. The V-I and V-T behavior of the theick films YBCO samples of figure 1 indicating a high Tc and and a low Jc.

The consistency of high crystalline quality at high growth rates under photo-assisted MOCVD is challenging when related to the poor critical current values extracted for the samples. These are transport Jc values measured by application of pulsed currents through the samples. The possibility of poor crystalline quality at the atomic level has been studied under a TEM investigation of atomic quality of the YBCO film and of the interface regions. Figure 7a shows the TEM results of a selected area diffraction pattern of the bulk of the substrate LAO/YBCO film interface region showing excellent crystalline orientation between the substrate and the YBCO film. Figure 7b. shows a SEAD pattern of the bulk of the YBCO film indicating excellent thick film crystalline order. In selected areas in the bulk of the YBCO thick film (fig. 7c), some streaking is observed implying the existence of stacking faults at the interface. On the whole, however, the TEM indicates extremely high crystalline quality for the YBCO thick film.



a. b. c.

Figure 7. Selected area diffraction patterns of YBCO film/LAO substrate region (a.); of the interior of the YBCO film (b.); and of a region of the interior of the YBCO film showing streaks due to stacking faults.

TEM bright field images further confirmed that the sample surface and interface regions were highly ordered. The bright field data confirms stacking faults at the interface with, however, a sharp interface between the YBCO and the substrate. In addition, the top surface of the YBCO samples is seen to be well structured with no defects supporting the SEM data of high-density YBCO films.

This recent data supports the hypothesis that large thickness films of YBCO can be successfully grown with extremely high crystalline quality. The poor Jc characteristics of the films, however, can only be supported by the proposal that the films are SO GOOD that there are not enough pinning centers in the films to prevent flux flow, and hence result in low Jc.

Further development of thick YBCO films grown on $LaAlO_3$ substrates has yielded YBCO films of over 15µm thickness. The YBCO were grown by photo-assisted MOCVD utilizing a single precursor liquid delivery source system..

The YBCO films of up to 15 µm thickness have exhibited very high crystalline quality as shown in Figure 8. The SEM micrograph of the fracture cross section of the same film shows high a density films with no voids.The surface morphology of the film indicates a dense surface with some large precipitates. The precipitates occur only on the surface of the YBCO and do not permeate into the bulk, indicating that they are probably due to the termination of the growth process of PhAMOCVD.

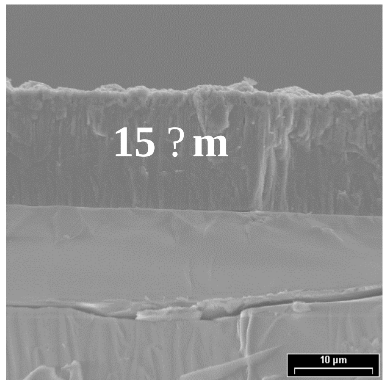
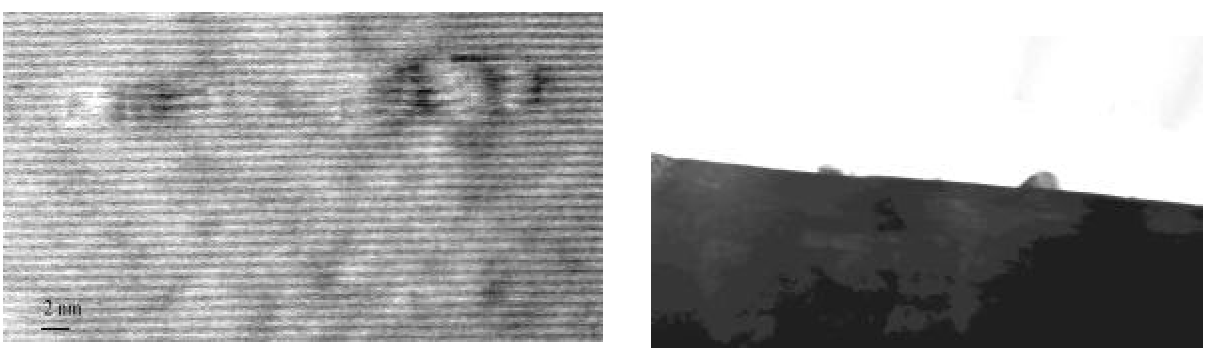


Figure 8. Micrographs of the cross section of a 15 ? m thick YBCO film.

The high resolution transmission electron microscopy (HRTEM) studies of a 10? m thick YBCO film show excellent crystalline quality for the YBCO with however some lattice strain near the YBCO/LAO interface (Figure 9a). This strain field is probably caused by the lattice miss-match of the YBCO with the LAO. It is also well to note from Figure 9b that the area at the surface of the film and the particle structure on the surface shows a sharp demarcation clearly indicating that the surface particles are in fact on top of the surface and can be rightly called precipitates not penetrating into the bulk of the sample.



a. b.

Figure 9. HRTEM micrographs for a 10 ? m thick YBCO.

The ultra-high crystalline quality of the thick films, however, does not obviously support the measured Jc data which in Figure 4 shows Jc ~ 4 x 10^5 A/cm^2 – much lower than expected for a high crystalline quality film. It is well documented that YBCO films must be crystallographically oriented to have high Jc. The data of figure 3, however, revives our previous proposal that PhAMOCVD films may simply be TOO crystallographically perfect, and hence do not have enough pinning center to realize high Jc.

To support this assumption, we have taken one of the thick film YBCO samples (a 4? m sample reported on earlier) and have generated additional pinning center through bombardment of the sample with 1 MeV protons to a does of 3 x 10^{14} protons/cm^2. The results of this pinning center generation can be seen in Figure 10 where the Jc for the sample has increased by a factor of ~6 due to the bombardment. It should be noted here that the Jc measurement system has a anomalously high noise level, which is being addressed, hence the rather large voltage reading in the Jc/V curve. Further work is underway to repeat this data set, and to generate additional pinning centers by higher dose and/or higher energy proton bombardment.

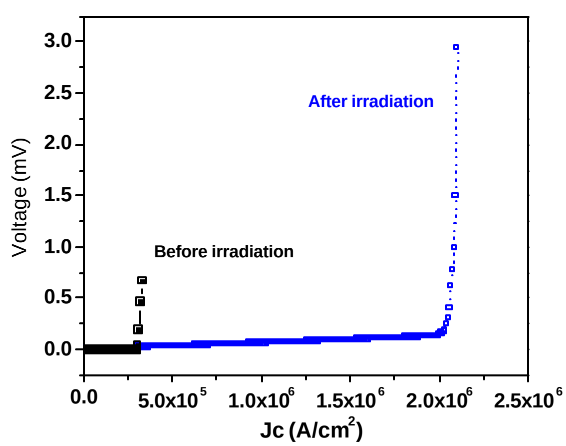


Figure 10. Jc behavior of a 4? m thick YBCO sample before proton irradiation, and after proton irradiation. Note increase of Jc by a factor of 6.

Based on PEER Review comments concerning Jc measurement, the Jc measurement system has been re-analyzed and found to have a major problem in the computer interface. The Jc system was upgraded in FY-04 with the addition of a new pulsed current power supply and a computer interface for data acquisition. The data acquisition board was found to be of inappropriate specs for low noise detection of voltage. This resulted in a high noise level well above 1 ?V. The computer A to D board also generated a voltage offset signal yielding a positive slope to the measured I-V curve.

The system is in the process of being upgraded by replacement of the A to D card with a Keithly 820 nanovolt meter, the purchase of a high current pulsed power supply and development of a LabView program to control the current ramp of the system. Preliminary data show that the samples previously tested showing a high voltage signal and a signal with an increasing slope no longer show those properties although there is still about 5 ? V of voltage noise (Fig 11.). The current Jc system now shows Jc's of the order of 1.5 x 10^6 A/cm^2 for 5 ? m thick YBCO samples grown on $LaAlO_3$.

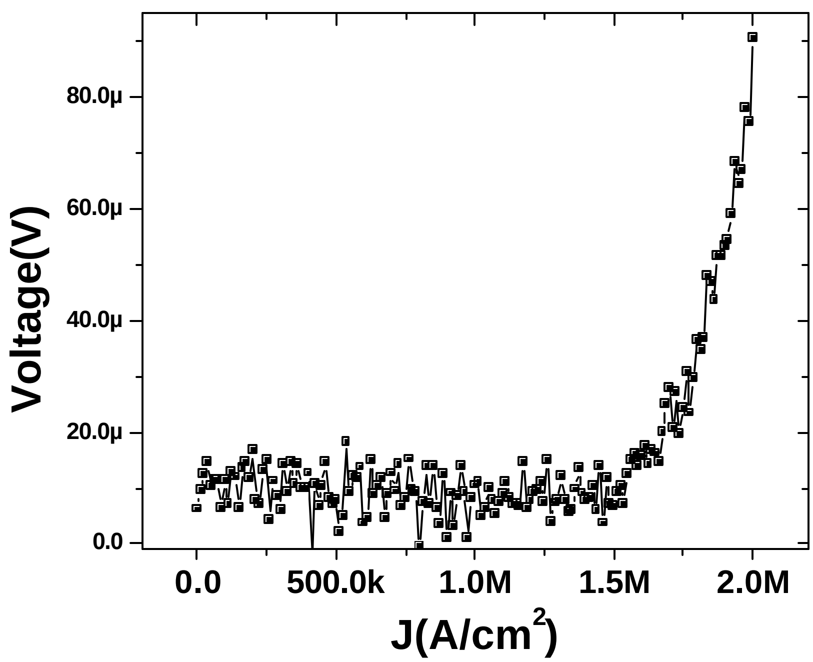


Figure 11. Jc measurement for 5 ? m thick YBCO film on $LaAlO_3$.

Further optimization and reduction of noise is underway, with the expectation that <1 ? V noise levels will soon be achieved.

Second year funding has not been received; hence only limited effort has been afforded the program. The Jc measurement system has been tuned to yield noise at a level of < 1? V, and only a two additional thick film samples have been fabricated since new precursors have to be purchased to continue additional growths. YBCO at ~ 5 ? m has been grown on LAO substrates with the usual ultra-high crystalline quality. Trapped field measurements have however, yielded signs of microcracks in the film. This will be further investigated.

Patents: None

Publications/Presentations:

Jianming Zeng, Jie Lian, Luming Wagn, Penchu Chou, and Alex Ignatiev, "HRTEM Characterization of $YBa_2Cu_3)_{7-x}$ Thick Films of $LaAlO_3$ Substrates", Physica C, **405**, 127-132 (2004).

Jianming Zeng, Irene Rusakova, Zhongjia Tang, Xin Zhang, Dalber Candela, Alexander Molodyk, Naijuan Wu, And Alex Ignatiev, "$YBa_2Cu_3O_{7-X}$ Thick Films Deposited By Photo-Assisted Metal-Organic Chemical Vapor Deposition", Presented at: 5th International Conference on New Theories, Discoveries and Application of Superconductors and Related Materials, Chongqing, China, July 2004.

A. Molodyk, X. Zhang, J. M. Zeng, and A. Ignatiev, "The Development of Thick Film YBCO for Coated Conductor Applications", Presented at: 5th International Conference on New Theories, Discoveries and Application of Superconductors and Related Materials, Chongqing, China, July 2004.

A. Ignatiev, "Superconductivity and Its Impact on Our Use of Energy", Chongqing University Plenary Lecture at the 2nd Anniversary of eth Chongqing Institue for Superconductivity, Chongqing , China, July 2004.

Milestone Status Table:

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments
1	Jc Decrease Study			
1.0	Grow Thick YBCO Films on LAO	2/20/04		Series of thickness under study
1.1	Analyze YBCO Microstructure	8/30/04		Microstructure analysis underway
2.1	Measure Electrical Properties	8/30/05		Electrical characterization underway
3.0	Grow Thick YBCO Films on RABiTS	5/15/05		Await Substrates from ORNL
4.0	Analyze YBCO Microstructure	11/15/06		**Not completed due to program termination**
3.1	Measure electrical Properties	2/20/07		**Not completed due to program termination**
5.0	Develop Jc Model for YBCO/LAO	5/30/07		**Not completed due to program termination**

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments
5.1	Develop Jc Model for YBCO/Ni	8/30/07		**Not completed due to program termination**
6.0	Address Jc drop mitigation	8/30/07		**Not completed due to program termination**
6.1	Fabricate High Jc Thick Films	8/30/07		**Not completed due to program termination**
7.0	Present Final Report	8/30/07		**May 10, 2006**

Budget Data as of 5-10-06:

			Spending Plan		
Phase / Budget Period			DOE Amount	Cost Share	**Total Allocated**
	From	To			
Year 1	10-1-03	9-30-04	$75,000	0	**$75,000**
Year 2			$75,000	0	**0**
Year 3			$75,000	0	**0**
Year 4					
Year 5					
		Totals	$225,000		**$75,000**